

# Effects of Excess Iodine and Water on Bunsen Reaction for Over-Azeotropic Limit

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## Abstract

Phase separation is of major importance in a Bunsen reaction in sulfur-iodine thermochemical cycle for hydrogen generation. Extensive experimental data on Bunsen reaction was collected and assembled over range of reaction temperature 293 - 393.5 K, excess iodine in the range of 1-16 moles, and excess water in the range of 1- 22 moles. The data was systematically analyzed to see key parametric effects on the reaction. The effects of iodine, water and temperature were studied on density ratio, distribution of components in two phases, reverse Bunsen reaction, SO<sub>2</sub> dissolution, and azeotrope limits. Best operating conditions were obtained to for which Bunsen reaction would be economical. The analysis indicated that iodine excess of 4 to 6 moles, water excess of 10.5 to 12.5 moles, and temperature range of 345-360 K are the best operating range for the Bunsen reaction. These operating ranges ensure no side reaction, economical operation by avoiding excess iodine, water and complicated options to break or bypass azeotrope. In addition reverse Bunsen and SO<sub>2</sub> solubility study are also considered for better understanding of process. Based on this study unique points of operation are recommended.

## Keywords

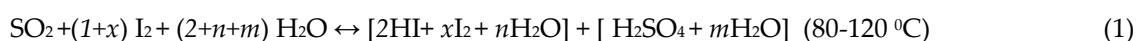
*Bunsen Reaction; Phase Separation; Hydrogen Production; Iodine-sulfur Cycle; Azeotrope*

## Introduction

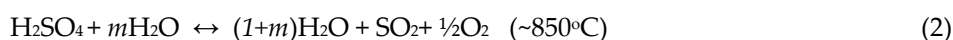
The sulfur-iodine (SI) cycle is one of the most promising thermo-chemical water splitting technologies for large scale production of hydrogen. There are various methods for hydrogen production including electrolysis, steam-methane reformation, direct photo-catalytic, and thermochemical processes. The General Atomics (GA), Sandia National Laboratories (SNL) and the University of Kentucky (UK) have examined earlier literature on thermo-chemical processes that offer potential for efficient, cost effective, large scale production of hydrogen by water splitting with high temperature heat input from advanced nuclear reactor (Norman 1981, Brown *et al* 2003). Their evaluation concluded that sulfur-iodine thermochemical water splitting cycle is the best method for large scale hydrogen production using high temperature heat from nuclear reactor.

The SI process consists of three major chemical processes as shown in Figure 1, resulting in direct dissociation of water into oxygen and hydrogen. These processes are as follows:

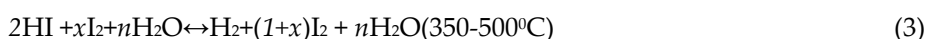
Bunsen reaction (Section I):



Sulfuric acid decomposition. (Section II):



Hydriodic acid decomposition (Section III):hydriodic acid



Reaction (1) is Bunsen reaction where iodine, water and sulfur dioxide reacts to form sulfuric acid and hydriodic acid which occurs at low temperature. Reactions (2) and (3) are decomposition reactions that occur at high and medium temperature respectively that decompose sulfuric acid (SA) and hydriodic acid (HIx). Here  $\text{SO}_2$ , water and iodine are recycled and  $\text{H}_2$  and  $\text{O}_2$  are taken out as product.

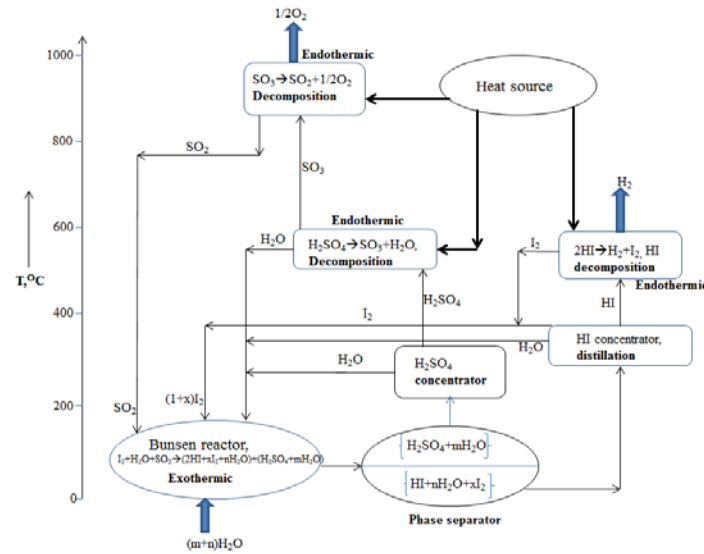


FIGURE 1. SCHEMATIC OF SI CYCLE

In reaction (1),  $x$  and  $(n+m)$  are excess iodine and water required for Bunsen reaction, that ends up in SA and HIx phase after Bunsen reaction and during phase separation. Excess iodine and water are crucial for making the process spontaneous, exothermic and for reduction of contamination. Although the excess water in the Bunsen process helps to make this process thermodynamically favorable, the exothermic processes at low temperature causes high irreversibility due to the large negative change in the Gibbs free energy leading to a significant energy loss. The heat released at low temperature cannot be effectively recovered and the irreversible process reduces the cycle efficiency (Revankar and Oh 2005).

There are side reactions that depend on temperature and content of iodine and water (Sakurai *et al* 2000a). The side reactions are shown in equations (5) and (6),



Side reactions should be avoided, as it may unbalance the cycling material or clog the pipes and hamper the downstream processing. Norman *et al* (1981, 1982) have reported operating conditions for Bunsen reaction with higher values of iodine and water excess, because of unavailability of sufficient data.

The Bunsen reaction and phase separation include only liquid phases and no catalyst. Phase separation is also simple process based on density difference and is not affected by the type and volume of liquid or size of equipment. It is confirmed by Kim *et al* (2012) that there is no effect of reactor shape and length on Bunsen reaction and phase separation. Bunsen reaction and phase separation are exclusively function of iodine, water excess,  $\text{SO}_2$  and temperature. Hence all the published data could be easily combined, as there is neither need for considering catalyst activity and variation of catalyst nor any of components in Bunsen reaction that act as catalyst.

Liquid-liquid equilibrium (LLE) phase separation characteristics, distribution of major components in two phases namely sulfuric acid phase (SA phase) and Hydriodic acid (HIx phase) is of major concern. SI cycle can be made economical by reducing the iodine and water excess in feed for Bunsen reaction to reduce the cost of downstream processing for their recovery.

The present work is limited to conventional Bunsen reaction and does not consider electrochemical Bunsen reaction (Nomura *et al* 2005, Immanuel *et al* 2012) where electrochemical cell is used and phase separation is facilitated with a membrane. Lee *et al* (2008) have analyzed the experimental data and have recommended an

optimal window of operation for Bunsen reaction and phase separation. However after Lee *et al* (2008) work there is a substantial amount of new experimental data on Bunsen reaction available in the literature (Maatouk *et al* 2009, Yoon *et al* 2009, Giaconia *et al* 2009, Parisi *et al* 2011, Zhu *et al* 2012, 2013, Kim *et al* 2013, 2014, Ying *et al* 2013, Zhang *et al* 2014). The data was systematically analyzed to arrive with precise operating range and with over-azeotropic conditions for cost effective SI cycle operation on the path of commercialization and to avoid costlier and complicated routes (Giaconia *et al* 2009).

The present work includes relevant experimental data for unique elaborate study on azeotrope and SO<sub>2</sub> effect, and reverse Bunsen reaction. The data is systematically analyzed to arrive at very precise operating conditions for over-azeotropic operation with respect to iodine and water excesses and temperature. In addition recent literature on reverse Bunsen and SO<sub>2</sub> solubility are examined for better understanding of process and recommendations are made for unique optimal single point of operation in addition to more precise range.

## Previous Work

Sakurai *et al* (1999) studied the effect of iodine in feed on two phase separation at 273K. The phase separation was reported to have initiated at 0.32 molar fraction of iodine in the feed and improved as iodine fraction in feed increased to 0.43. Below the lower limit of iodine content, phase separation did not take place. Above an upper limit, iodine solubility became saturated and excess iodine solidified. Sakurai *et al* (2000b) extended this study to wider temperature range to investigate effect of iodine and temperature in HI/H<sub>2</sub>SO<sub>4</sub>/I<sub>2</sub>/H<sub>2</sub>O solution on LLE phase behavior at 273~368K. Their major findings were: (a) increase in iodine content improves the liquid-liquid separation characteristics by reducing impurities in both phases, and (b) increase in temperature improves the iodine solubility by widening allowable iodine range.

Sakurai *et al* (2000b) studied the possibility of side reaction in HI/H<sub>2</sub>SO<sub>4</sub>/I<sub>2</sub>/H<sub>2</sub>O solution at 273K ~368K. The two possible side reactions with hydrogen iodide and sulfuric acid as reactants are formation of solid sulfur and hydrogen sulfur gas. The driving force for both side reactions are high temperature, high HI concentration, and low excess iodine. Excess moles of iodine were recommended to be between 4.41 and 11.99 to prevent side reaction in lower bound and iodine solidification at higher bound.

Lee *et al* (2005, 2006) investigated the effect of water on H<sub>2</sub>SO<sub>4</sub>/HI/H<sub>2</sub>O equivalent to 0.047/0.093/0.860, 0.038/0.075/0.887, 0.030/0.061/0.909 at 293K. Unlikely from Sakurai *et al* (2000b) H<sub>2</sub>S formation was the main focus. Increase of water content in feed from 0.86 to 0.909 aided to reduce H<sub>2</sub>S formation; however, 2-phase separation was not observed after the further increase from 0.92 in water content. It is important to select certain water range to prevent undesired product formation and process two-phase separation at the same time.

Kang *et al* (2006) investigated the phase separation behavior of H<sub>2</sub>SO<sub>4</sub>/HI/H<sub>2</sub>O/I<sub>2</sub> = 1/2/14~20/0.5~8.0 from 298 K ~ 353K. The lowest impurity level in both HI phase and H<sub>2</sub>SO<sub>4</sub> phase was obtained at the highest iodine mole excess of 8.0 and the highest temperature of 353K. As iodine in feed increases, water in HI<sub>x</sub> and H<sub>2</sub>SO<sub>4</sub>, respectively, reduces and then increases. The opposite trend occurs as temperature increases. The physics behind the trend is temperature aids affinity of HI<sub>x</sub>-H<sub>2</sub>O water system but iodine reduces affinity of HI<sub>x</sub>-H<sub>2</sub>O.

Giaconia *et al* (2007) performed series of experiments with H<sub>2</sub>SO<sub>4</sub>/HI/H<sub>2</sub>O/I<sub>2</sub> with 4~16 moles of iodine range and 11~16 moles of water, at 353.15K, 368.15K, and 393.15K. Their study concluded (a) increase in iodine has a little impact on impurity in both phases unless high iodine in feed is added, and (b) temperature also has marginal effect on purity in both phases (c) no sulfur formation was observed (d) optimal condition to enhance exothermic condition and economical operation are, 353.15 K with 3.9 moles of excess iodine.

Lee *et al* (2008) performed collective studies from the experimental data of Sakurai *et al* (2010b), Giaconia *et al* (2007), Kang *et al* (2006), and Lee *et al* (2005) to arrive at their own optimal operating range. The suggested optimal range was 4~6 moles of excess iodine, 11~13 moles of excess water, and 330K ~ 350K of temperature range. The optimal iodine excess of 4 was selected as lower bound because of the sulfur formation issues. An upper bound of 6 moles of excess iodine was proposed because too high iodine excess leads to increase in separation cost in downstream. Lower bound of 11 moles of excess water was defined as to minimize water content to maintain HI concentration above azeotrope. An upper bound of 13 moles of excess water was defined because the HI

concentration became lower than azeotrope above 13. In terms of temperature operating range 330K was selected as lower bound to improve exothermic characteristics of Bunsen reaction and 350 K was selected as upper bound to widen iodine operating range.

Maatouk *et al* (2009) did preliminary experiments at 308K to study phase separation with iodine variation 1-4.2 mole excess while water excess from 10-35. The conclusion of their study was (a) Increase of iodine will help in better separation (b) iodine prefers HIx phase showing density variation between two phases (c) diminishing water in system favors liquid phase separation.

Zhu *et al* (2012) studied the effects of iodine and temperature on quaternary system seeking optimal range. The experiment was carried out in molar ratios of  $\text{H}_2\text{SO}_4/\text{HI}/\text{I}_2/\text{H}_2\text{O}$  equivalent to  $1/2/n/12$  at 291 K ~ 358K and iodine of 1-6 moles excess fixing other moles. The temperature range of 345 K ~ 358K and 2.45~3.99 moles of excess iodine were proposed as the optimal range because HI remained well above azeotropic concentration.

Kim *et al* (2013, 2014) studied concept of counter Bunsen reaction and continuous phase separation using counter current flow reactor. Their results showed feasibility of this technique. The impurities reductions in HIx and SA phase were comparable to batch process of phase separation though it offered marginal advantage because of counter current  $\text{SO}_2$  gas flow.

### Parametric Study

Extensive literature data were collected where the focus of experimental study was on Bunsen reaction and separation. The main data sets are referred with an alphabets corresponding to the references as given in Table 1.

TABLE 1. ABBREVIATIONS USED FOR AUTHORS USED IN GRAPHS

Author Described Alphabet	References
A	Sakurai <i>et al</i> (2000b)
B	Kang <i>et al</i> (2006)
C	Yoon <i>et al</i> (2009)
D	Giaconia <i>et al</i> (2007)
E	Zhu <i>et al</i> (2012, 2013)
F	Maatouk <i>et al</i> (2009)

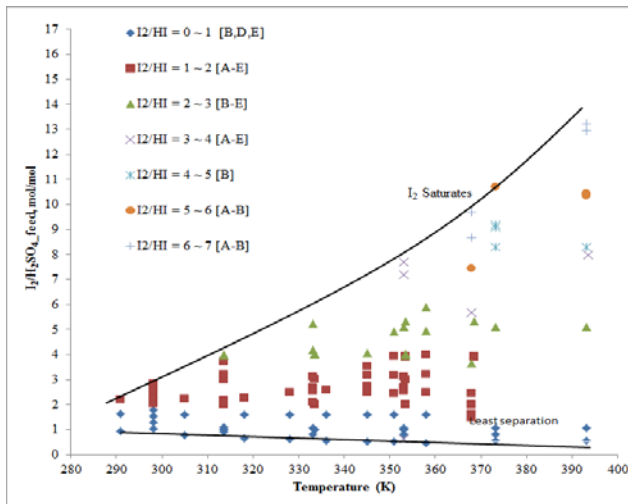


FIGURE 2. TEMPERATURE VERSUS ALLOWABLE IODINE FEED RANGE AS LIQUID-LIQUID SEPARATION CHARACTERISTICS AT 291 K - 393.5 K

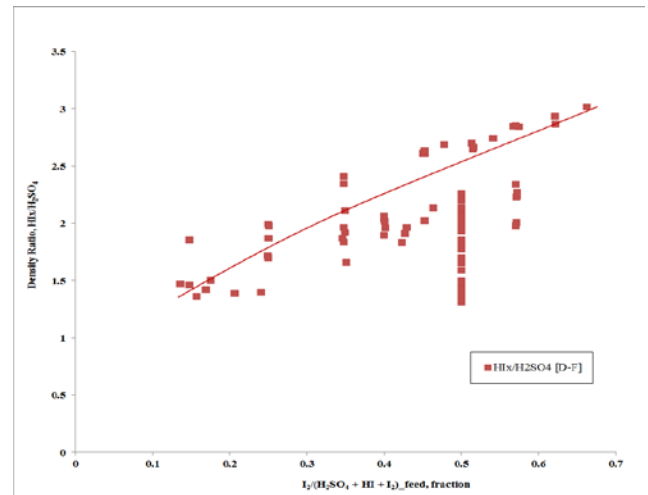


FIGURE 3. EFFECT OF IODINE FRACTION IN FEED ON DENSITY RATIO OF HIx AND SA PHASES

### Limits for Iodine Solubility

The allowable iodine range as function of temperature is represented in Figure 2. Iodine excess in each group of  $\text{I}_2/\text{HI}$  ratio was plotted against temperature. The upper bound represents iodine saturation limit and lower bound represents the least amount of excess iodine in feed to cause liquid-liquid phase separation. It is very clear from

the data that temperature has minimal effect on lower bound but has significant effect on upper bound. Higher temperature helps to dissolve more iodine in the feed that causes the improvement in the separation of phases. This understanding allows one to use iodine solubility compared to higher temperature of iodine melting and to choose best operating condition at lower temperature.

### Iodine Effect

The data from literature [D-F] have been plotted for evaluation of density variation in two phases as function of iodine in feed and the graph shows the clear trend as shown in Figure 3. The density ratio widens as iodine content in the feed increases. Iodine has found to affect HIx phase density more than the SA phase and hence the ratio was observed to improve dramatically. The density ratio of HIx phase to SA phase increase from 1 to 3.3. It could be clearly observed from Figs. 4 and 5 that iodine in HIx phase increases with improvement of iodine in feed whereas it diminishes in SA phase. This leads to enhancement in density of HIx phase more rapidly than SA phase and hence density ratio was observed to improve.

SA phase contain HI and I<sub>2</sub> as contaminants as they severely affect the decomposition and concentration process in H<sub>2</sub>SO<sub>4</sub> section. HI and I<sub>2</sub> can also poison the catalyst used in H<sub>2</sub>SO<sub>4</sub> decomposition section (O'Keefe *et al* 1980). Hence it is crucial to reduce HI and I<sub>2</sub> in SA phase. The contamination in SA phase was observed to reduce drastically with improvement of iodine excess in feed as shown in Figure 4.

Contamination of HI in SA phase was observed to reduce from 0.5 mol ratio to 0.05, approximately 10 times reduction of initial amount in feed as iodine excess increases from 1 to 4. After iodine excess of 4, the reduction is marginal. The iodine and water contamination in SA phase were also observed to reduce drastically with increase in iodine excess in feed up to 4 mole excess and then diminish gradually. Iodine contamination was observed to diminish from 0.18 mol ratio to approximately zero in SA phase as iodine goes from 1 to 4 moles excess in feed whereas water was observed to reduce from mol ratio of 14 to 4. Hence iodine excess in feed of 4 could be considerable lower limit of operation; it will be more clearly shown as lower limit in further discussion.

Iodine excess in feed also has similar effect on components in HIx phase as shown in Figure 5. Figure 6 shown in ternary diagram depicts iodine addition widening the separation gap and improves the phase separation by reduction of contaminants.

H<sub>2</sub>SO<sub>4</sub> and water contaminations in HIx phases were observed to diminish with increase of iodine in feed. H<sub>2</sub>SO<sub>4</sub> contamination was observed to reduce from approximately 1 mol ratio to zero whereas water was observed to reduce from 8 mol ratio to 2 and then increase gradually after iodine excess of 4. Iodine content in HIx phase was observed to increase with increase of iodine excess in feed and it would cause the huge separation cost in downstream processing to recover and hence iodine excess in feed need to be optimized for economic operation

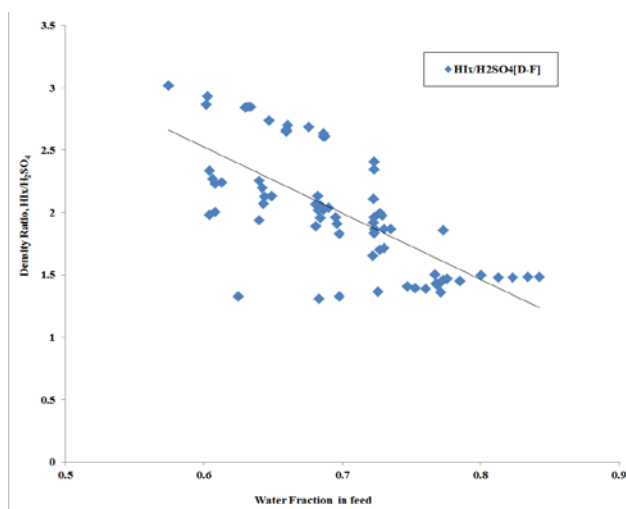


FIGURE 4. EFFECT OF IODINE EXCESS IN FEED ON COMPONENTS IN SA PHASE

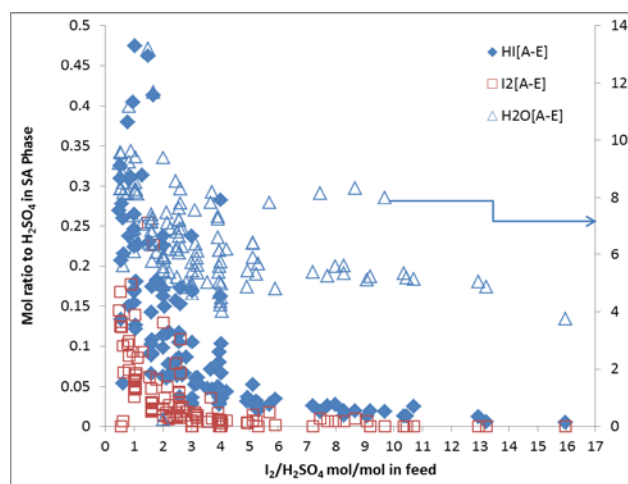


FIGURE 5. EFFECT OF IODINE EXCESS IN FEED ON COMPONENTS IN HIX PHASE

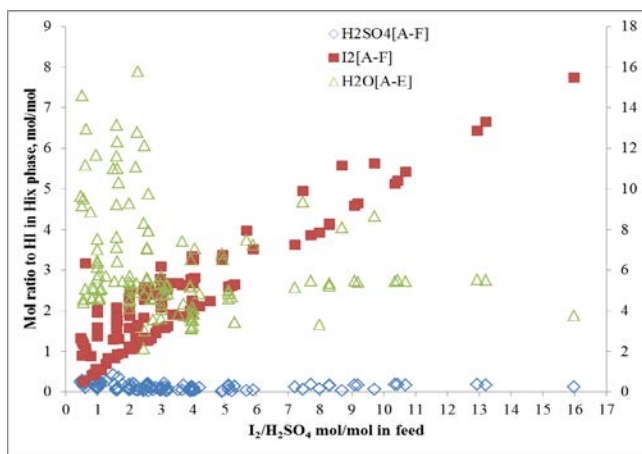


FIGURE 6. EFFECT OF IODINE ON ALL PHASES TOGETHER IN TERNARY DIAGRAM AT 314K

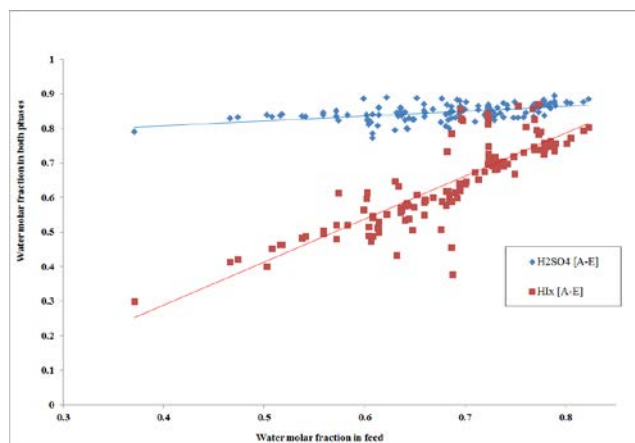


FIGURE 7. EFFECT OF WATER FRACTION IN FEED ON DENSITY RATIO OF HIX AND SA PHASES

### Water Effect

It is also crucial to define precise water excess for economical operation. The effect of water in feed on the density ratio in two phases was shown in Figure 7. The density ratio was observed to reduce from 3.3 to 1 as water fraction in feed improves from 0.6 to 0.85. The water prefers HIX phase over the SA phase causing dilution of iodine and HI, hence reduction of density ratio of two phases as shown in Figure 8.

Figure 9 demonstrates the effect of water in feed on contamination in HIX phase. It was observed that increase of water will initially reduce the contamination and then fails to continue after some point. Water makes process exothermic and spontaneous and iodine helps for separation. Water supports reduction of contamination up to 12.5% and then dilution of iodine dominates, weakening the liquid-liquid separation effect. This leads to increase in contamination in both phases. Excess water will be penalizing in downstream process in term of extra heat required for removal. Hence water need to be optimized to make overall process economical and effective.

### Temperature Effect

Temperature has peculiar role in Bunsen reaction and phase separation. Figure 10 gives effect of temperature on contamination. The contamination was observed to reduce with increase of temperature. The iodine solubility improves with increase of temperature and hence reduces the contamination. The impurities of HI (data considered with absence of water) in SA phase was observed to reduce from 27 % to 2 % as temperature increases from 291K to 393.5 K. It is clear from Figure 2 that increase in temperature increases the iodine solubility and iodine is responsible for better separation. Hence it is expected and observed in all the temperature graphs that temperature increase causes more iodine dissolution in feed and more iodine in feed will have better separation and hence reduction in the impurities.

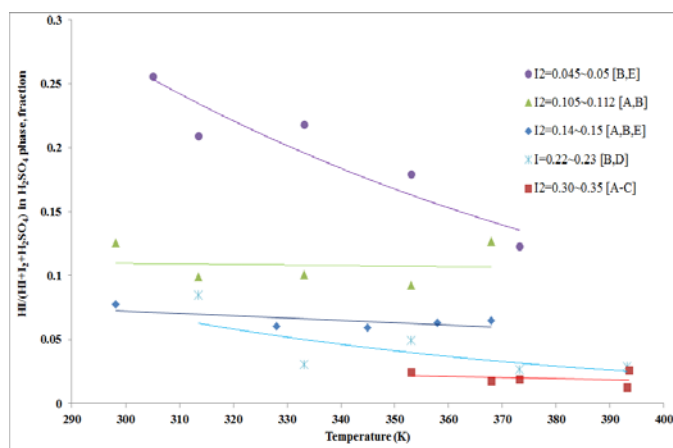


FIGURE 8. WATER DISTRIBUTION IN BOTH PHASES

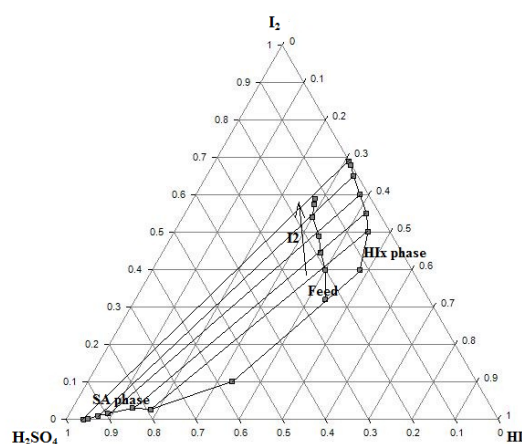


FIGURE 9. EFFECT OF WATER IN FEED ON CONTAMINATION IN HIX PHASE



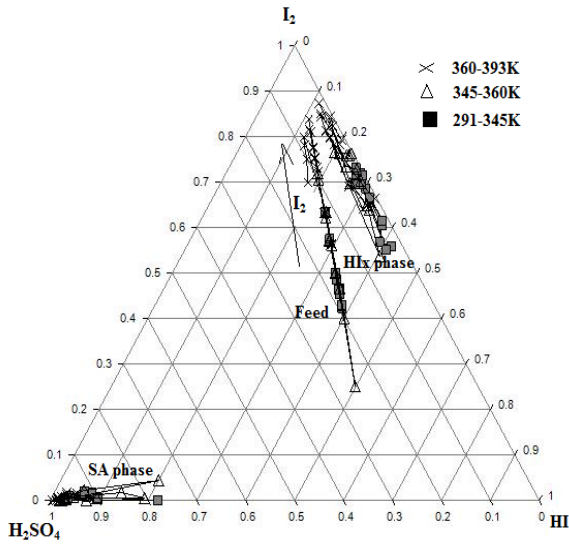


FIGURE 10. EFFECT OF TEMPERATURE RANGE ON CONTAMINATION IN SA PHASE

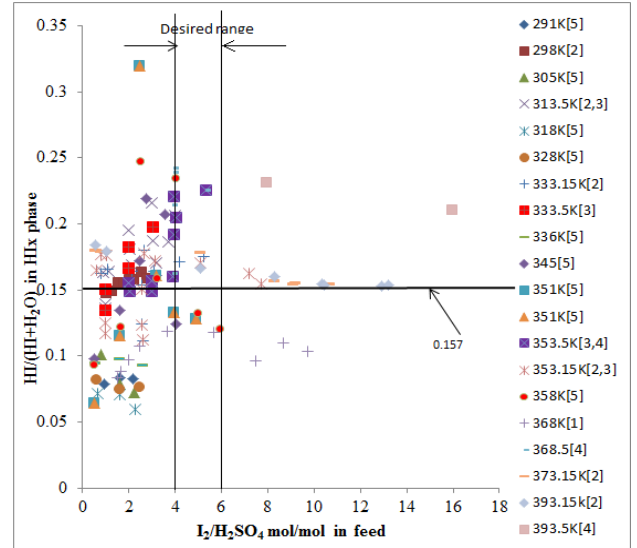


FIGURE 11. EFFECT OF TEMPERATURE ON ALL PHASES COMPONENT AT GLANCE IN TERNARY DIAGRAM

Temperature has marginal effect in increasing reaction rate of Bunsen reaction but major effect is on iodine solubility. Hence it would be wise decision to choose temperature on higher side to get advantage of better reaction rate and higher iodine inclusion to get better phase separation. The higher the temperature, higher would be iodine and better would be separation but process cost would go up and downstream processing will become expensive because of additional cost for removal. Hence the middle temperature range and iodine range would be best to have energy efficient and effective process in term of reducing contamination and downstream process economy. Figure 11 in ternary diagram shows the same conclusion that increase of temperature leads to intake of more iodine and hence improves separation.

### Optimal Range

It is now, distinctly clear that we need to choose best operating condition in term of iodine, water excess in feed and operating temperature range. Appropriate choice should make Bunsen reaction and phase separation and downstream processing contributing to whole SI cycle to be economical and effective. Henceforth efforts are directed towards confirming very precise operating conditions for above mentioned parameters.

### Reverse Bunsen Reaction

In HIx phase, reverse Bunsen reaction was observed to reduce the HI fraction and increase in I<sub>2</sub> fraction. Yoon *et al* (2009) have explained the probable reason for this with 4 reactions. Equations 5 and 6 have already described two side reaction and following equations (7) and (8) specify the remaining



Reaction (7) could be avoided by maintaining oxygen free atmosphere. Reaction (8) is reverse Bunsen reaction that is endothermic in nature. Reaction (5) and (6) are the side reactions. The reverse Bunsen reaction being endothermic in nature was observed to be prominent at higher temperature. Figure 12 shows reduction in loss of HI and generation of I<sub>2</sub> at higher iodine excess. It could be observed that there is significant reduction in loss of HI and generation of I<sub>2</sub> as iodine improves from 1 to 4 mole excess in feed.

Low iodine excess shows higher formation of iodine, confirming side reactions and reverse Bunsen reaction. Bai *et al* (2009, 2013) have studied reverse Bunsen reaction and have concluded that higher temperature favor formation of SO<sub>2</sub> and I<sub>2</sub> by reverse Bunsen reaction compared to sulfur or H<sub>2</sub>S formation in the side reaction. So it can be concluded that low temperature and high iodine content will subsidies reverse Bunsen reaction and side reaction. Therefore it gives us first hint for lower limit of iodine excess for best operating condition. However additional experimental work is required to check reverse Bunsen reaction at high iodine content.

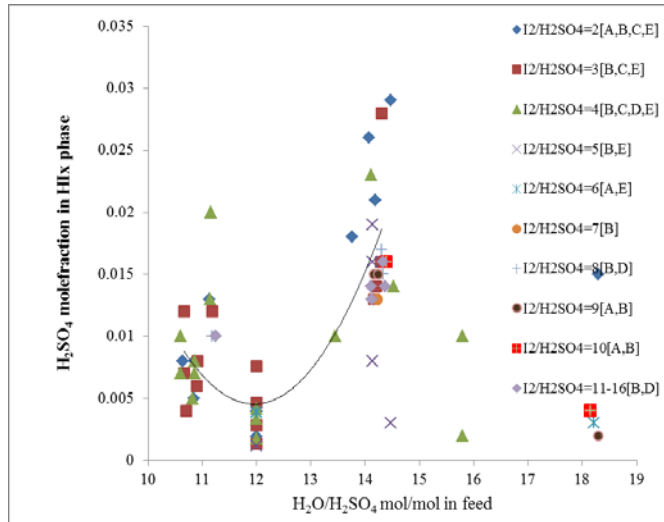


FIGURE 12. EFFECT OF IODINE IN FEED ON REVERSE BUNSEN REACTION

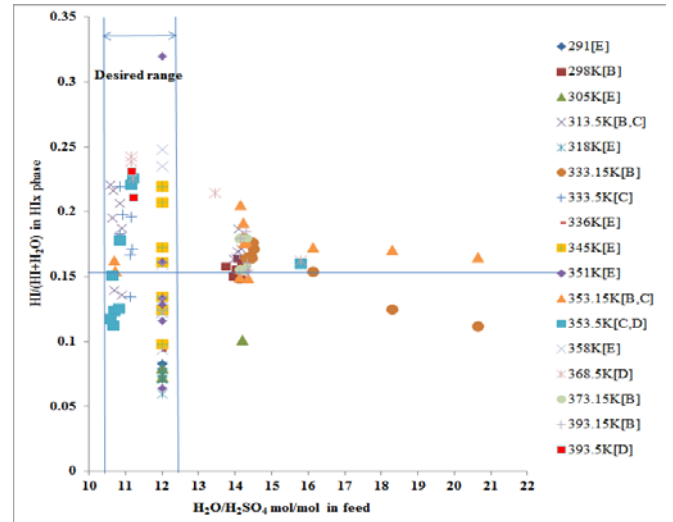


FIGURE 13. EFFECT OF IODINE ON AZEOTROPIC COMPOSITION IN HIX PHASE

### Azeotropic Study

Figure 13 shows effect of iodine excess in feed on the HI/(HI+H<sub>2</sub>O) mole fraction in the HIX phase with corresponding temperature. Azeotropic mole fraction of HI in HIX phase is 0.157. The overall literature temperature range data were analyzed for this purpose. At lower iodine range, possibility of HI/(HI+H<sub>2</sub>O) mole fraction to be above minimum azeotropic mole fraction was more, as low iodine and low water excess would be involved. But as iodine excess less than 4 was reported to have problem of sulfur formation (Sakurai *et al* 2000a) and reverse Bunsen reaction (Yoon *et al* 2009).

Hence iodine excess above 4 was considered to be useful region. The HI/(HI+H<sub>2</sub>O) fraction could be seen to 0.17-0.24 (above azeotropic point) for iodine excess of 4-6 respectively and after these points over-azeotropic fraction points were minimal. Moreover higher iodine concentration will make downstream processing of iodine removal uneconomical. Hence iodine excess of 4 to 6 could be seen as best region to operate to keep system operation to get HI/(HI+H<sub>2</sub>O) fraction above azeotropic mole fraction. This will also aid to avoid the costly options i.e. reactive distillation (Norman 1981), electro-dialysis (Onuki *et al* 2000, Hwang *et al* 2003, Kasahara *et al* 2004), and HI extraction by phosphoric acid (O'Keefe *et al* 1982, Giaconia *et al* 2009) for bypassing azeotrope. The corresponding suggested temperature range based on azeotropic graph is 345-360K, where observed iodine range falls. So observation of low temperature favors the HI/(HI+H<sub>2</sub>O) fraction to be above azeotropic composition is in agreement with conclusion made by Yoon *et al* (2009) and Zhu *et al* (2012).

Figure 14 shows the effect of water excess in feed on the HI/(HI+H<sub>2</sub>O) in HIX phase with respective temperatures. Water prefers HIX phase compared to SA phase. Hence if water excess in feed is minimized, it will lead to desired fraction of HI to be over azeotropic point. It was observed from distribution of data, 10.5 to 12.5 form the region of choice, as it has maximum points for HI/(HI+H<sub>2</sub>O) falling above the azeotropic fraction and also region of lowest contamination as confirmed in Figure 9. Water excess of 14 also shows another favorable point but consideration of this point has disadvantage on improvement in impurities as shown in Figure 9 leading to downstream processing uneconomical. The optimal range selected for water corresponds to temperature range of 345-360K which is in agreement with optimal range observed for iodine effect.

### Contamination in Phases

Figures 15 and 16 show effect of temperature on contamination in HIX and SA phase with respect to different iodine mole excess in feed. Both figures show that the minimum contamination falls within temperature range of 345-360 K. Higher temperature and iodine amount shows higher reduction in contamination of 0.01 fraction compared to 0.02 fraction at proposed temperature. Higher temperature would not be good choice, as it will lead to excess energy requirement for present Bunsen reaction and more cost involved for recovery of iodine in downstream process. For clear understanding of best operating conditions the minimum contamination points



reported at respective temperature corresponding to iodine excess were considered. Figure 17 shows the effect of temperature on lowest contamination points in HIx phase and its % reduction in HIx phase. Percentage reduction is calculated with fraction of maximum reduction of contamination occurred considering all data. It can be observed from the data that minimum contamination for  $\text{H}_2\text{SO}_4$  in HIx phase lies in temperature range of 345-360K.

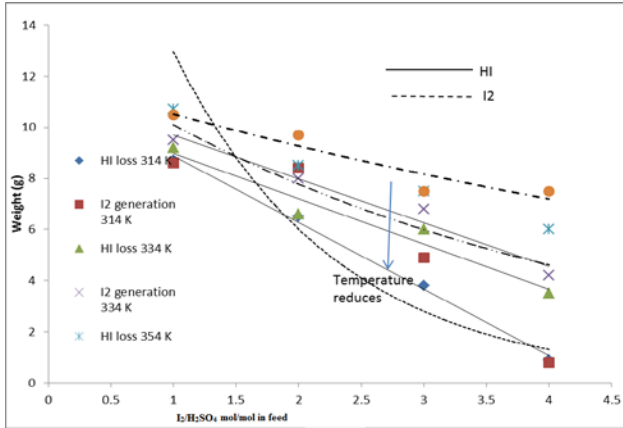


FIGURE 14. EFFECT OF WATER ON AZEOTROPIC COMPOSITION IN HIX PHASE

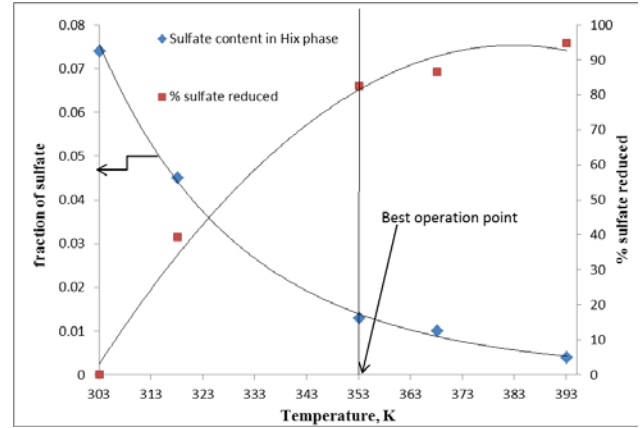


FIGURE 15. EFFECT OF TEMPERATURE ON CONTAMINATION IN HIX PHASE AT DIFFERENT IODINE EXCESS

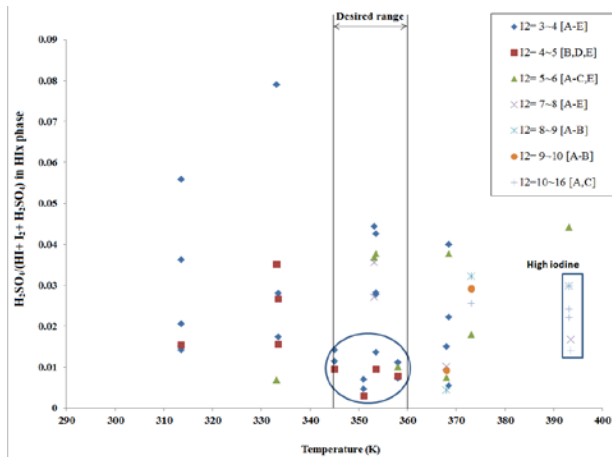


FIGURE 16. EFFECT OF TEMPERATURE ON CONTAMINATION IN SA PHASE WITH RESPECT TO IODINE EXCESS

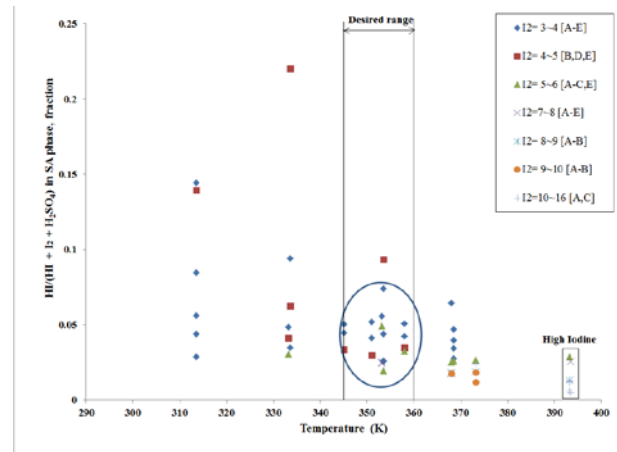


FIGURE 17. EFFECT OF TEMPERATURE ON IMPURITIES IN HIX PHASE AND % REDUCTION FOR LOWEST CONTAMINATION POINTS

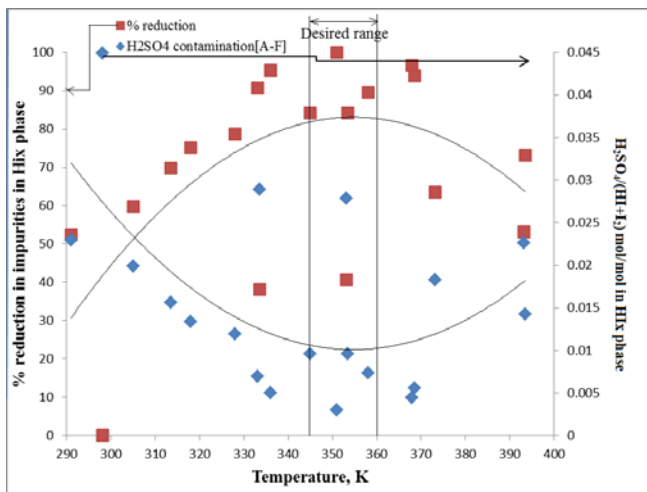


FIGURE 18. EFFECT OF TEMPERATURE ON CONTAMINATION IN HIX PHASE AND IODINE FOR LOWEST CONTAMINATION POINTS

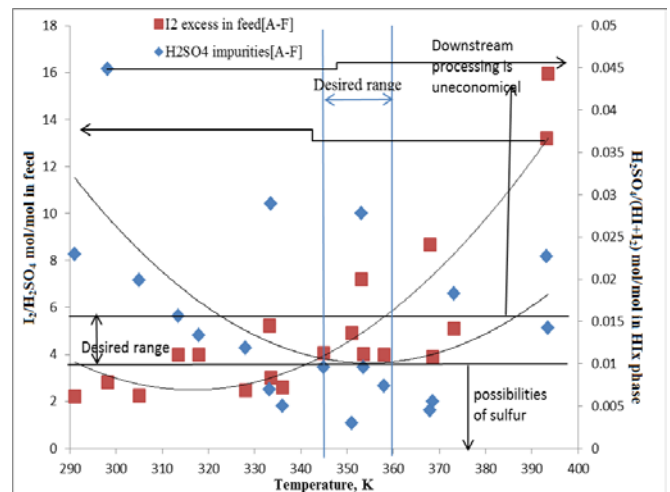


FIGURE 19. EFFECT OF TEMPERATURE ON CONTAMINATION IN SA PHASE AND % REDUCTION FOR LOWEST CONTAMINATION POINT

Figure 18 illustrates the effect of temperature on the  $I_2$  excess in feed corresponding to the lowest contamination points in HIx phase. The iodine excess of 4-6 was found to be best operating condition as below 4 there is strong possibility of side reaction and above 6, downstream processing becomes uneconomical. Above the iodine excess of 6, demand for high temperature and excess iodine, will make process uneconomical.

Figure 19 shows the temperature effect on lowest contamination points and % reduction of impurities in SA phase. The contamination in SA phase also shows that up to 85% of reduction in contamination was achieved in temperature range of 345-360K. Increasing temperature demands for additional cost at benefit of merely 10-15% improvement though majority of % reduction of impurities was found at desired temperature range.

Figure 20 shows the effect of temperature on lowest contamination points in SA phase and  $I_2$  excess. The data confirms the range of temperature 345-360K to be optimum and iodine excess at 4-6 range. Below this range side reaction possibility is high (Sakurai 2000a). Figure 11 shows all the contaminations of 3 phases at glance in ternary diagram. This diagram uses the lowest contamination points available at different temperatures. The temperature range of 291-345K has low iodine hence less reduction in contamination. However, it was clearly observed that above 345-360K range there is substantial increase in iodine excess and reduction in contamination is marginal. Therefore 345-360K was reconfirmed as best temperature operating ranges in ternary diagram.

### SO<sub>2</sub> Effect

Parisi *et al* (2011) studied the effect of temperature on SO<sub>2</sub> absorption. It was observed that solubility of SO<sub>2</sub> reduces with increase in temperature. This study concludes SO<sub>2</sub> to be the stoichiometric bottleneck for Bunsen reaction. High temperature reduces the solubility of SO<sub>2</sub> in feed and Bunsen reaction being exothermic favors low temperature, results in diminishing the SO<sub>2</sub> conversion.

The temperature was found to reduce the sulfate contamination in HIx phase in SO<sub>2</sub> study as shown in Figure 21. The percentage reduction was calculated considering reduction at 303K to be 0% reduction and highest temperature giving maximum reduction and all the reduced content were compared with this as fixed value. It was found that approximately 85% reduction in contamination occurred as temperature rises from 303K to 353K. Temperature changes from 353K to 393K does not reduce the contaminant to great extent, it rises from 85 to 95%. Hence the 353K was concluded to be the best temperature for the operation of the Bunsen reaction to make process more economical considering the downstream processing cost and operating cost for Bunsen reaction.

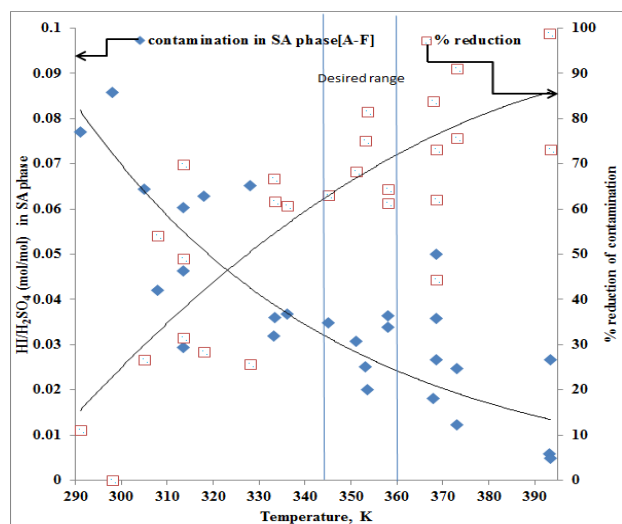


FIGURE 20. EFFECT OF TEMPERATURE ON CONTAMINATION IN SA PHASE AND IODINE FOR LOWEST POINT OF IMPURITIES

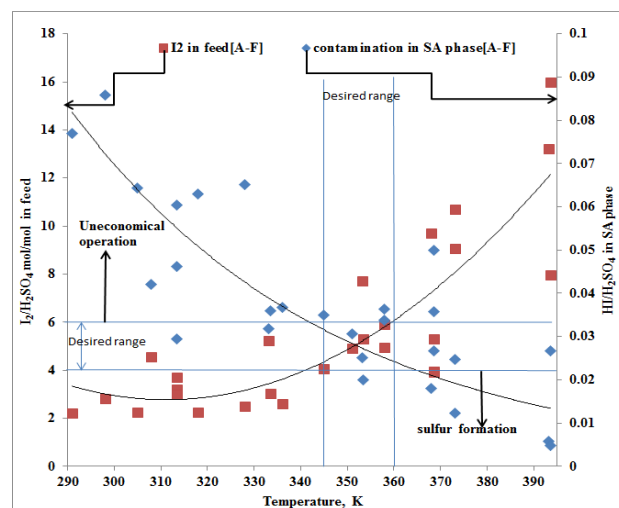


FIGURE 21. EFFECT OF TEMPERATURE ON SULFATE CONTAMINATION IN SA PHASE WITH RESPECT TO SO<sub>2</sub> ABSORPTION

### Best Operating Conditions and Comparison with Operating Range in Literature

By studying the data on excess water in SA and HIx phase for various temperature conditions an optimal operating range can be chosen. The mole fraction of water in SA and HIx phase was given in term of individual mole as follows

$$u = m / ((K^*x + K^*y + K^*z) + m) \quad (9)$$

$$v = n / ((L^*x_1 + L^*y_1 + L^*z_1) + n) \quad (10)$$

where K and L are total moles of SA and HIx phase whereas x, y, z and x<sub>1</sub>, y<sub>1</sub>, z are mole fraction of HI, H<sub>2</sub>SO<sub>4</sub> and I<sub>2</sub> in SA and HIx phase respectively.

$$m + n = I \quad (11)$$

where I is moles of water in feed.

$$K + L = F \quad (12)$$

where F is moles of feed.

So in all we have four equations and 4 unknown hence can be solved to find out individual moles of water going into both the phases.

The water mole excess going in SA and HIx phases were calculated for lowest points of contamination at different temperatures. It was found that 353.5K temperature point with iodine mole excess of 4, results in lowest fraction of water moving to HIx phase i.e. 48% and making azeotropic ratio of 0.2 which is in agreement with the results by Giaconia *et al* (2007) and Parisi *et al* (2011). Hence it confirms 353.5K and iodine excess of 4 and water excess of 10.8 to be best single operating point for acceptable over-azeotropic composition and low contamination.

Table 2 gives comparison of present study with best operating conditions suggested by literature published data. Present study has come up with very precise operating range and optimal point of operation. Recent experimental study on azeotropic composition Zhu *et al* (2012, 2013), SO<sub>2</sub> absorption study Giaconia *et al* (2007) and reverse Bunsen reaction study [19] were guideline for precise operating conditions. Norman *et al* (1981) had chosen melting point of iodine as operating temperature at 393K and then soon the temperature was lowered to 293-373 (Norman *et al* 1981); however excess water was used in their operating conditions. Giaconia *et al* (2007) had optimized operating range but it appeared closer to lower bound specified by Sakurai *et al* (2000a). Kubo *et al* (2004) has good temperature range but prefer more excess water. Lee *et al* (2008) studied experimental data to present optimal window with lower temperature range specified of 330-350 K. Present study considers recent experimental work including azeotropic range, SO<sub>2</sub> absorption, and reverse Bunsen reaction and suggest a precise operating range of 345-360 K for whole SI cycle to be economical.

TABLE 2. COMPARISON OF PRESENT STUDY WITH LITERATURE FOR OPTIMAL RANGE

Operating parameter	Present study		Lee <i>et al</i> (2006)		Norman <i>et al</i> (1981)	Norman <i>et al</i> (1982)	Giaconia <i>et al</i> (2007)	Kubo <i>et al</i> (2004)
	Optimal	Range	Optimal	Range				
T, K	353.5	345-360	330	330-350	393	293-373	353	343
x	4	4-6	4	4-6	8	7.6	7.6	4.4
m+n	10.8	10.5-12.5	11	11-13	14	14.7	14.7	24.6
m	5.18	6	5	5	4	4.1	4.1	8.9
n	5.62	5-7	6	6-8	10	10.6	10.6	15.7

## Conclusions

The systematic analysis of experimental data includes study of contaminations, distribution of components, azeotropic compositions in both SA and HIx phase with respect to variation of iodine and water excess in feed and temperature. It also included reverse Bunsen reaction and effect of SO<sub>2</sub> on Bunsen reaction and contamination. It was concluded that temperature range of 345-360K and iodine excess of 4-6 would best operating range. The SO<sub>2</sub> effect also confirms the reduction of 85% impurities at 353.15 K temperature, in coordination with above optimal temperature range. The ternary graph also reconfirms optimal range and it was observed that there is no significant advantage at higher temperature range. The water excess in feed of 10.5 to 12.5 was found to be precise optimal range after study of contamination reduction in SA and HIx phase and azeotrope. Due to limited studies additional experiments are required to study the reverse Bunsen reaction at higher iodine and temperature to reconfirm their absence at higher operating range of temperature and iodine. Additional experiments would also

be beneficial to understand SO<sub>2</sub> effect at different iodine and water excess to get complete and elaborate idea of its exact effect in Bunsen reaction as it seems to be stoichiometric bottle neck.

#### ACKNOWLEDGMENT

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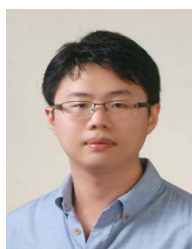
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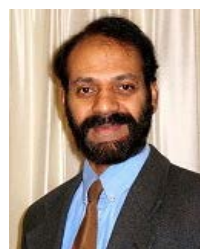


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